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BLOCKAGE OF FLAME CONTROL DEVICES: DESIGN AND
MAINTENANCE CRITERIA

R. P. Wilson, Jr., et al

Arthur D. Little, Incorporated

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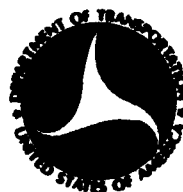
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BLOCKAGE OF FLAME CONTROL DEVICES:
DESIGN AND MAINTENANCE CRITERIA

R. P. WILSON, JR.

P. G. GOTT



FINAL REPORT

AUGUST 1975

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The contents of this report reflect the views of the authors, who are responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policy of the Coast Guard. This report does not constitute a standard, specification, or regulation.


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16. Abstract A study was conducted of the blockage of flame control devices and the effect of flow constriction on the pressure-relief function of the venting system. It was found that the open area must be almost completely blocked before the tank pressure would rise significantly (e.g., 93% blockage to produce 3 psig at 30 ft/sec normal venting speed). The available evidence suggests three blockage mechanisms occur with significant frequency: (a) plugging by liquid cargo due to condensation or overflow; (b) polymerization of monomer-type cargoes; and (c) corrosion by cargo vapor or moist air. Seven cargoes were found to present a significant polymerization hazard (acrylate and methacrylate esters, formaldehyde, acrylonitrile, butadiene, styrene, vinylidene chloride, and vinyl acetate) the characteristics of these materials were tabulated along with recommended use of inerting or inhibitors. The corrosion potential of 50 cargoes used with each of 20 metals was evaluated; out of 1000 combinations at least 130 were found unsuitable, with magnesium- and copper-based metals accounting for 90% of the unsuitable cases.					
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I. BACKGROUND

Venting systems are used on marine cargo and fuel tanks to relieve pressure differences which arise between the tank and its surroundings. If a flame control device presents too great a flow constriction, it becomes blocked and the pressure-relief function of the venting system fails.

This blockage hazard and its control are being analyzed by ADL as part of Contract No. DOT-CG-42357-A. Based on this study, ADL has determined some of the probable causes of venting system blockage and has set up guidelines which may be used by both regulatory agencies and venting system designers to minimize this hazard. Our findings are presented in this report, along with supporting data.

This study is intended to be used as background information for design, inspection, and maintenance of cargo tank venting systems.

II. EFFECT OF BLOCKAGE ON VENTING SYSTEM PERFORMANCE

A. Pressure Buildup due to Blockage

Blockage is here defined as an area constriction in a cargo tank venting system. Area constrictions from film accumulation along the walls of vent pipes are very unlikely to be significant. A constriction is more likely to develop locally at a flame screen, flame arrestor, or PV valve. It may be a reduction in the free flow area or may also take the form of a valve stuck so that it cannot fully open. For a "typical" venting system, we will show that the amount of area constriction needed to cause an overpressure problem in a tank is on the order of 95 percent.

Consider a vent pipe running from a cargo tank into a partially blocked flame control device. The tank is being loaded with a liquid cargo, and the flow velocity in both the filling and venting pipes is typically 10 feet per second.^{(1)*} (Total area of vent lines must, by A.B.S. practice, be at least 125% of total area of fill lines). Design guidelines indicate that fill pipes are sized to give a liquid velocity of about 10 ft/sec. This velocity is corroborated by the data on vent area (A) for given cargo tank volume (V) when it is assumed that the entire tank must be filled in about 12 hours. That is, one can derive a velocity $V(12 \text{ hr})/A$ for any tanker design; these velocities cluster around 10 ft/sec. Martin⁽⁷⁾ gives a normal range of venting velocities of 10-30 ft/sec and discusses means to boost vent speeds to 100-200 ft/sec.

Consider Figure 1. Area A_1 is the flow area of the vent pipe; area A_2 is the flow area of the partially blocked flame control device.

*For the purposes of this analysis, we neglect the cargo vapor volume compared to the air volume; at stoichiometric fuel/air ratio, the vapor volume is about 5% of total for most organic cargoes.

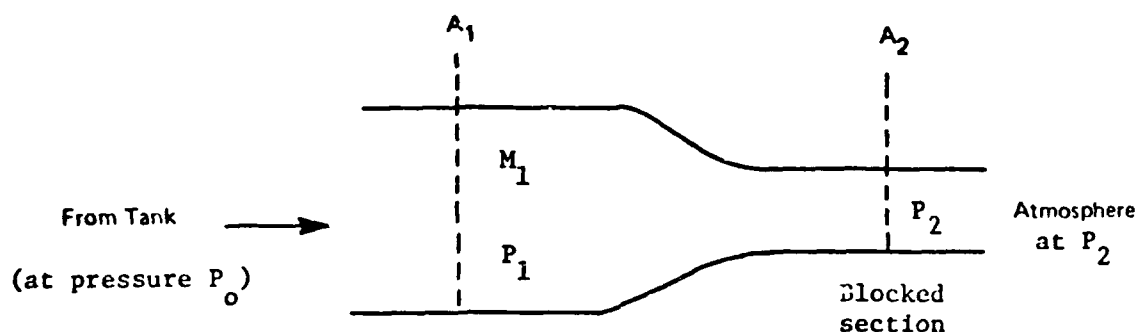


FIGURE 1

Since the occlusion is assumed to be local, we take the flow to be adiabatic during contraction. Following Shapiro⁽⁸⁾, the area ratio A_1/A_2 associated with a given pressure ratio P_1/P_2 for adiabatic flow is as follows:

$$\frac{A_2}{A_1} = \left(\frac{P_1}{P_2} \right)^{\frac{1}{k}} \left[\frac{\frac{k-1}{2} M_1^2}{\left(1 + \frac{k-1}{2} M_1^2 \right) \left(1 - (P_2/P_o)^{(k-1)/k} \right)} \right]^{1/2}, \quad (1)$$

where k is the ratio of specific heats (1.4 for air) and M_1 is the Mach number (velocity divided by speed of sound (1088 ft/sec for air) in the unobstructed section). Since venting speeds are 10-30 ft/sec in Section 1, we can make the approximations $\frac{k-1}{2} M_1^2 \ll 1$ and $P_1 \approx P_o$ (Shapiro⁽⁸⁾ gives $P_1/P_o = .9994$ for $M_1 = .03$). With these approximations, Equation (1) becomes

$$\frac{A_2}{A_1} = \left(\frac{P_o}{P_2} \right)^{\frac{1}{k}} M_1 \left(\frac{k-1}{2} \right)^{\frac{1}{2}} \left[1 - (P_2/P_o)^{\frac{k-1}{k}} \right]^{-1/2} \quad (2)$$

By substituting $M_1 = .01$ and $.03$, and $k = 1.4$ into Equation (2), it is possible to calculate the fractional free area A_2/A_1 associated with a given pressure rise P_2/P_o , for venting speeds of 10 and 30 ft/sec. Figure 2 presents the results of this analysis.

It is apparent from Figure 2 that the flow area of a venting system must be reduced to about 6 percent of the vent pipe area before a pressure differential of even 1 psig will occur in the tank (for 10 ft/sec venting

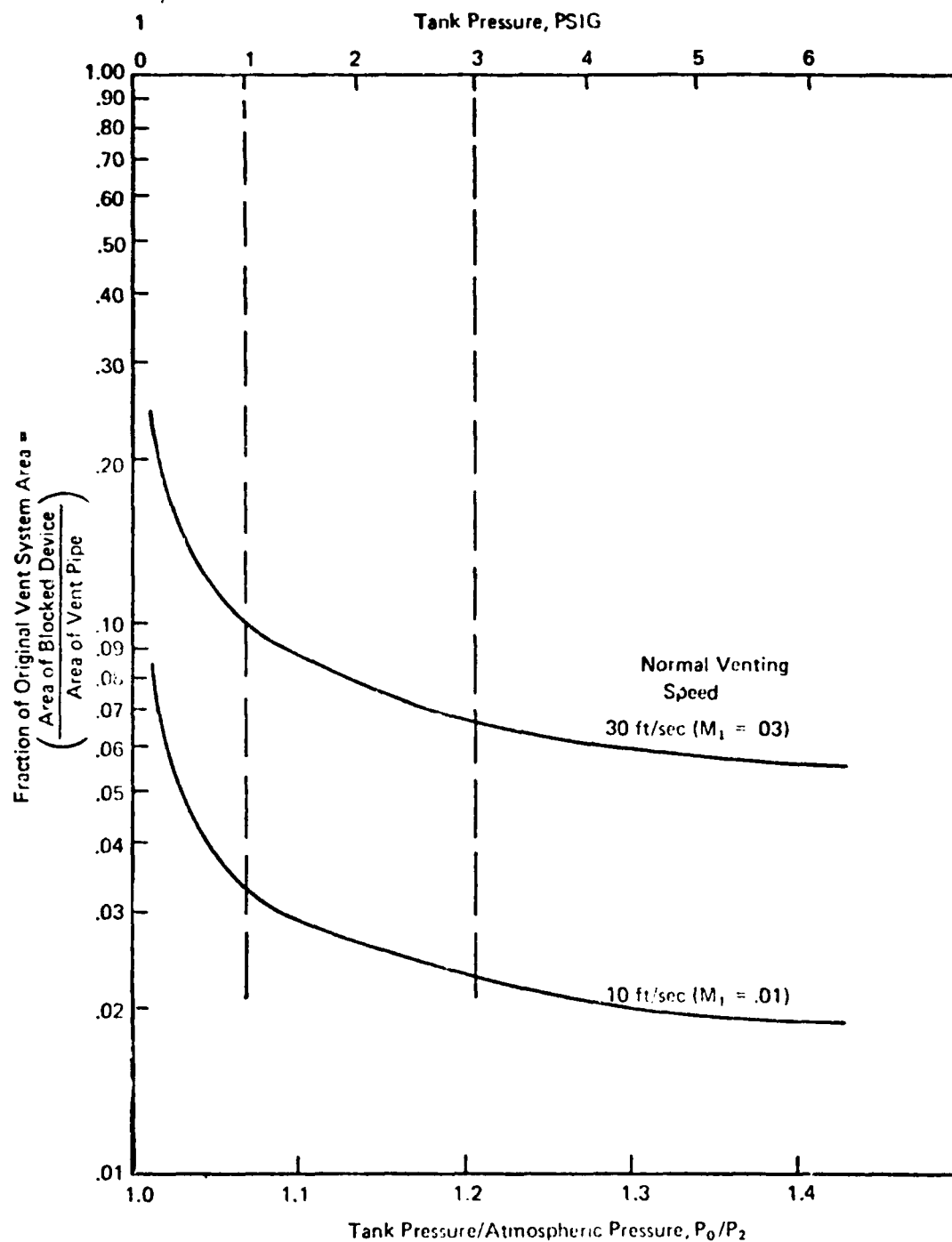


FIGURE 2 FLOW AREA REDUCTION VERSUS TANK PRESSURE

velocity). For 30 ft/sec venting velocity, the flow area must be reduced to about 10 percent of the vent pipe area. The probability of 96 percent blockage occurring in vent system components with large characteristic dimensions is obviously very low because the film buildup would have to be in the order of several inches. For flame control devices, however, the story is quite different. For instance, a typical flame screen having 40 wires per inch has openings approximately 1/60 of an inch square (.0167" x .0167"). Ninety-six percent area reduction of each passage would require a film only .0063 of an inch thick on each wire.

B. Effect of Blockage on Performance of Flame Control Devices

Task I of this study indicates that it is the small characteristic dimension of flame control devices that enables them to control or stop the passage of flames. Flame control device performance is independent of the materials of construction (within reasonable mechanical limitations) and we can therefore conclude that any coating on the surfaces of the device would not, by itself, hinder its operation. Blockage occurs by the formation of a coating which in turn reduces the flow passage area. Because the ability to control flame passage increases with a reduction in the characteristic dimension (flow passage area), the fire performance of a flame control device may actually be enhanced by blockage -- that is, of course, unless the coating formed on the device is flammable and/or produces hot droplets or sparks which could reignite the gas upstream of the device.

III. CONDITIONS WHICH LEAD TO BLOCKAGE

A. Marine-Industrial Evidence on Blockage

Very little is quantitatively known about the severity of the blockage problem or the relative frequency of blockage for different cargoes, venting system types, and conditions of operation. Instances of blockage are usually recorded only when an accident investigation traces the cause to the venting system, and this is extremely unlikely because the blocked component is often destroyed. Therefore, our approach has been to qualitatively identify some of the causes of blockage which have been encountered by manufacturers and inspectors. Without a much more extensive investigation, it is impossible to be more quantitative about the relative hazard of blockage.

A review of industrial accidents reported to the Manufacturing Chemists Association and visits to several Coast Guard Marine Inspection Offices revealed that two probable causes of blockage are corrosion and plugging due to the cargo.

Out of 1,988 industrial accidents of all types reported by the Manufacturing Chemists Association⁽²⁾ from 1962 through 1973, only 16 were the result of venting system malfunction. The frequency of occurrence of the major malfunctions was as follows:

Presence of cargo or foreign material in venting system	7
Polymerization of cargo in venting system	3
Corrosion of venting system components	3
Other (operator error, inadequate vents, etc.)	3

Appendix A presents typical case histories in the first three categories. Manufacturers of monomers confirm that polymerization can readily occur if appropriate preventative measures are not taken.

Experience at Coast Guard Marine Inspection Offices reveals a similar pattern. From visiting several stations, the causes of blockage most often cited were, in order:

1. Tar-like or oily cargoes cause plugging of flame screens or flame control devices, either by condensed vapors or by overflow during loading.

2. Corrosion of flame screens and/or malfunctioning valves. Electrolysis between dissimilar metals is a sometimes cause of blockage if allowed to progress for a period of years. The particular example of a brass flame screen in a steel casing was cited by more than one inspector.

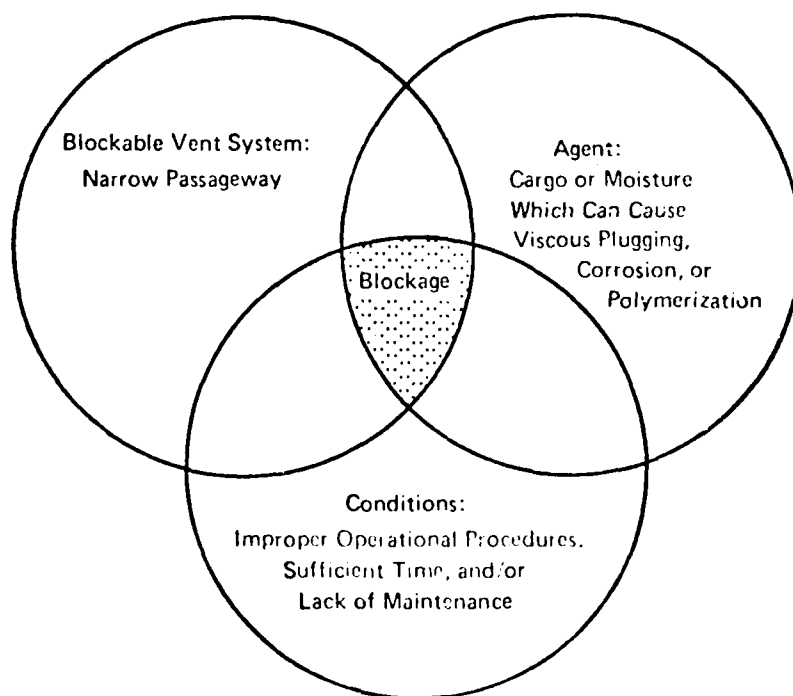
3. Unexercised pressure-vacuum valves, particularly those with beveled seats, bind up between inspections.

4. Painted flame screens.

As shown in Chapter II, for a given buildup of surface coating, blockage is most severe where individual flow passages are small, i.e., on flame screens. Polymerization blockage may occur in the less visible areas of venting systems. Corrosion is discovered most frequently on those components exposed to the weather but may also occur due to cargo vapor in less visible areas.

B. Factors Leading to Blockage

Blockage results from the direct obstruction of flow in narrow passages of the venting system by some foreign material. Three factors must be present before blockage may occur.



As we have seen, a vent system with small dimensions at at least one fitting appears necessary for blockage. When combined with a blocking agent and sufficient time and conditions for the agent to act, blockage may occur. The time is one very critical factor. Mechanisms such as corrosion act relatively slowly and in some cases may not produce significant blockage between inspections. Polymerization, on the other hand, is relatively rapid and could cause significant blockage while the vessel is in transit from one port to another.

Figure 3 is a "Fault Tree" detailing the various events which can lead to blockage. The bottom represents the root of the tree which is the occurrence of blockage by some basic mechanism. The chart may be read from the bottom up to determine the various causes of single blockage mechanisms, or from the top down to see where individual initiating phenomena may lead. The remainder of this section describes in greater detail the mechanisms by which factors such as corrosion and polymerization may act.

C. Agents Which Cause Blockage

Blockage due to film formation may be caused by several different agents. Table 1 categorizes the various agents which can lead to blockage. It is important to note that human and environmental agents, as well as the cargo, can individually or collectively act through various mechanisms -- chemical attack (corrosion), polymerization, deposition or freezing -- to cause blockage. Plugging and corrosion mechanisms appear to be the most common causes of blockage based on number of times cited by inspectors.

Improper maintenance procedures can cause either venting system blockage or "unblockage." Too-thorough paint jobs have been known to seal off vents by blocking flame screens. Unblockage has been discovered when in-service PV valves have been opened for inspection and their working parts found missing!

Condensation, ice, and air pollutant buildup are less severe causes of blockage. Ice is, of course, not permanent and easily spotted. Air pollutant buildup is a very slow process and usually

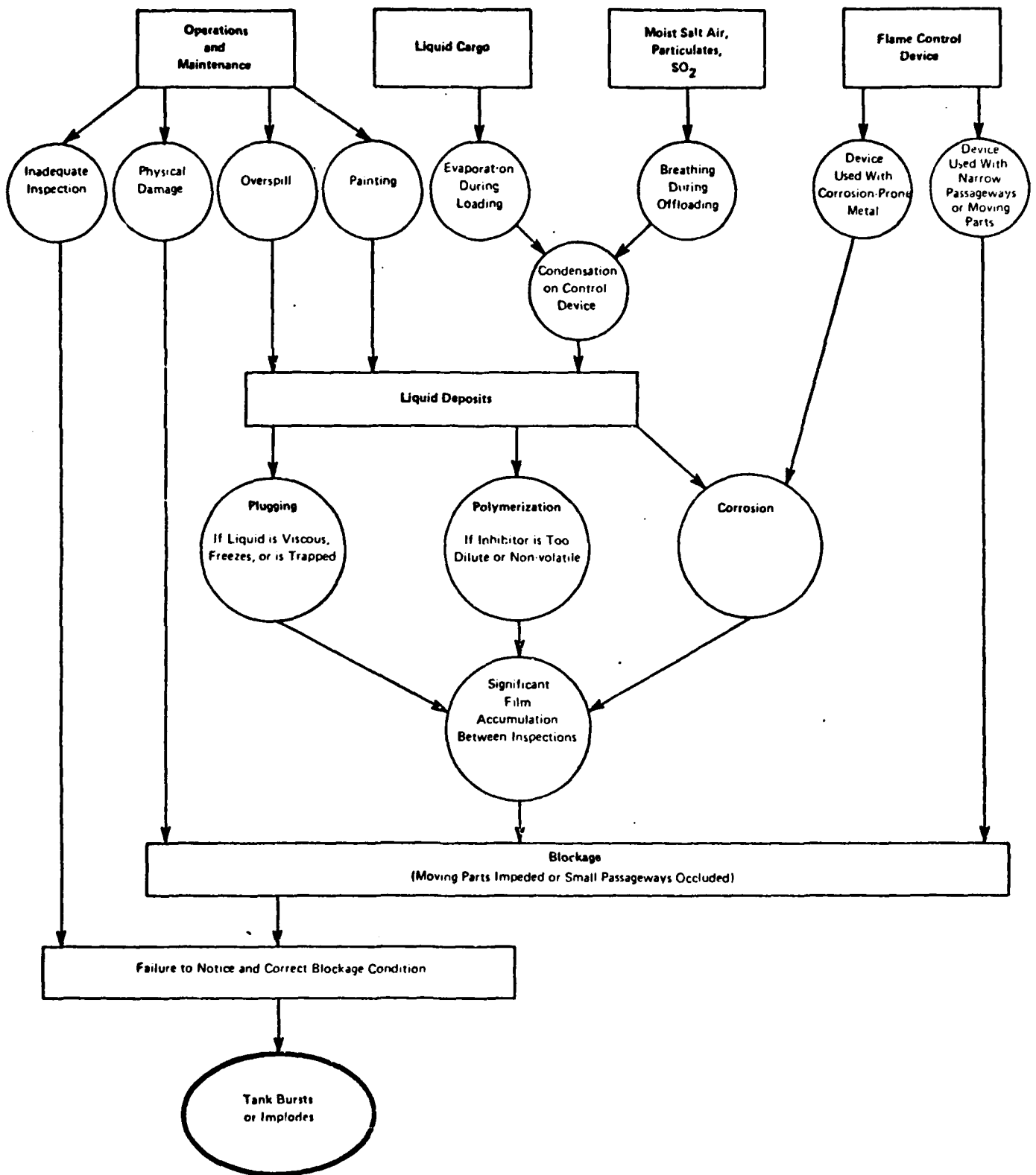


FIGURE 3 FAULT TREE FOR TANK FAILURE DUE TO BLOCKAGE

TABLE 1

Cause Film Build-up Mechanism	Environmental			Cargo		Human Operations (Handling or Maint.)
	Sea Spray Rain, Moist Air	Particulates	SO ₂	Vapor	Liquid	
Condensation	/		/	/		
Freezing	/				/	
Deposition	/	/		/	/	/ (Paint)
Polymerization		/		/	/	
Corrosion	/		/	/	/	
Physical Damage						/

presents no problems between venting system inspections.⁽⁵⁾ Condensation may sometimes cause liquid plugs to form in vent lines, but the effects can be minimized by providing drainage.

The possible mechanisms through which various agents may act are many. The exact mechanisms leading to blockage cannot at this juncture be pinpointed, however. Only an in-depth study of actually blocked venting systems can attempt to determine the exact causes of blockage. Let us examine more closely three often cited blockage mechanisms: plugging by the cargo itself, plugging by polymerized cargo, and corrosion.

D. Plugging by Cargo Deposits

Liquid cargo may reach venting system components by overfilling or by vapor condensation. This poses a blockage hazard in several ways.

If the cargo is viscous (e.g., tar or tarlike), film deposits could remain after an overspill, their thickness a function of surface tension and surface characteristics of the flame control device. Either a single application or repeated layers could build up to the point where the venting system is 90% or totally occluded. Oily mists from some cargoes are known to condense and build up layers as well. A particular problem can occur with molten cargoes. The vapors from these cargoes can enter a venting system, cool, crystallize, and form a solid plug.

Of the cargoes listed in subchapters D and O, two, molten naphthalene and sulfur, appear to have the potential for blockage by crystallization. These are presumably carried in insulated or heated tanks. (No special requirements are listed.) The vapors of these cargoes will travel into the venting system and crystallize there unless the venting system is maintained at temperatures above the melting point.⁽³⁾

Low points in venting systems or valves located below venting system outlets or inlets provide ideal collecting points for small amounts of liquids. Locations where condensate or other liquid might collect are avoided by proper design and, where they exist, should be

equipped with suitable means of draining the fluid. Liquid cargo can first collect in and plug these drains, allowing liquids to build up. These plugged drains can go unnoticed between inspections and over not too long a time allow sufficient liquid buildup on a valve to alter its set point considerably.

Liquid can also evaporate from these low spots, leaving solid or crystals behind. Eventually, this could form a solid plug in the venting system.

It is of interest to estimate the probability of venting system failure during the overspill itself, apart from the blockage problem. During overspill, the venting system becomes a liquid transport system rather than a gas transport system. To determine the pressure rise that may occur in such a situation, we will look at a hypothetical venting system. Let's assume that the only significant restriction in our hypothetical venting system is a PV valve, the tank is being filled with carbon tetrachloride, and all the venting is taking place through the properly designed venting system. The loading rate is 7204 ft³/hour, and the vent diameter is a nominal 6 inches (loading and venting flow velocity - 10 feet per second.) Under these conditions, a typical 6-inch PV valve will produce a tank pressure of approximately 2 inches of water (from a manufacturer's brochure)⁽³⁾ or .072 psi. If we assume that the PV valve acts like a nozzle⁽⁴⁾ we can write the equations for isentropic flow as follows:

$$V_g \approx \left[\frac{2G (P_o - P)_g v_g}{1 - .25(V_g/C)^2} \right]^{1/2}$$

$$\text{and } V_f = \left[2G(P_o - P)_f v_f \right]^{1/2}$$

where

V_f and V_g are the flow velocities of the venting liquid and gas respectively

G is the universal gravitational constant

P_o is the tank pressure (nozzle inlet pressure)

P is atmospheric pressure (nozzle outlet pressure)

v_f and v_g are the specific volumes of the venting liquid and venting gas respectively

C is the speed of sound

Considering that at these low velocities $\frac{v_g}{C}$ is almost zero, we can derive the following expression for the pressure drop if we assume that the venting velocity is independent of the phase. (This must be the case if the tank does not burst.)

$$(P_o - P)_f = (P_o - P)_g \frac{v_g}{v_f}$$

For air, $v_g = 13.3 \text{ ft}^3/\text{lb}$ and carbon tetrachloride, $v_f = .01 \text{ ft}^3/\text{lb}$; therefore, the pressure drop due to venting liquid would be

$$(P_o - P)_f = .072 \frac{13.3}{.01} = 96 \text{ psi}$$

We can see immediately that the venting of a liquid can create unacceptable tank pressures. The obvious preventative measures are to avoid overspill, install relief disks, and employ ullage hatches and sounding hatches as relief flow ducts.

E. Conditions for Corrosion

For materials utilized in the construction of the cargo tank and the venting system components close to it, the probability of metal corrosion is primarily a function of the corrosive properties of the cargo. For materials primarily in contact with the open air, such as those used at or near venting system outlets, the ability of the metal used to withstand corrosive attack from the marine and/or industrial air surrounding it is of primary importance. In between, corrosive attack could conceivably occur by the combination of the cargo with moisture and the various atmospheric pollutants that enter the venting system from outside.

1. Influence of Cargo Vapor and Liquid on Corrosion

Table 2 is a presentation of the corrosion potential of various cargo-metal combinations. The cargoes listed are those in subchapters D and O of Chapter 1, Title 46 Code of Federal Regulations, that have some potential for causing corrosion problems. For reference, they have been put into their respective Coast Guard reactivity groups.

TABLE 2

A: Total is satisfactory with this cargo; little or no corrosion will occur in a time interval equal to or greater than the inspection interval.

Blank: City insufficient or unavailable on metal-cargo combination.

Copper has been known to react explosively with gaseous acetylene in the presence of moisture. It should, however, be noted that in practice, copper and brass fittings are frequently used in acetylene systems with no ill effects.

F. Metal/cargo combination is not suitable due to the potential for severe corrosion between two-year inspection.

TABLE 2 (Cont'd)

[illegible]

FOOTNOTES FOR TABLE 2

1. Bronzes include commercial, aluminum, and phosphor bronze.
 2. 70/30 and 90/10 cupro-nickel alloys.
 3. Types 302, 303, 304, 316, and 420 specifically studied.
 4. Refers to all aluminums unless noted otherwise.
 5. Type 420 stainless steel - category "C."
 6. 90/10 cupro-nickel alloy - blank.
 7. 11000 series only; all others blank.
 8. Series 11000 and 3000 only; all other blank.
 9. Phosphor bronze - category "C."
 10. Series other than 1100 and 3000; category "D."
 11. Commercial bronze - category blank.
 12. Type 316 - category "C."
 13. 11000, 3000, 5000 series only; all other blank.
 14. 90/10 cupro-nickel - category "C."
 15. Series 4000 only.
 16. Aluminum bronze - category "A."
 17. Type 316 stainless - blank.
 18. Series 2000, 4000, 7000 - category "C."
- * Copper has been known to react explosively with gaseous acetylene in the presence of moisture. It should, however, be noted that in practice, copper and brass fittings are frequently used in acetylene torches with no ill effects.

The metals listed in the table are those which are commonly found in vent system components such as pipes, valves, and flame control devices.

Each square in the table matrix contains one of four different classifications - A, Blank, C, or F. These rate the metal cargo combinations from satisfactory to unsuitable based on corrosion data, as explained after the table.

This table has been compiled from literature and documented field experience. Entries in the table are on a worst case basis. That is, entries in the cargo columns indicate the performance of the worst of either the pure cargo or the cargo contaminated with water or sulfur dioxide.

It is evident from Table 2 that certain cargo groups are corrosion prone with most metals (e.g., I, XIV, XVI), and that certain metals corrode with most cargoes (e.g., magnesium and silicon brass).

2. Influence of the Marine-Industrial Air on Corrosion

Entries in the very last column of Table 2 consider the performance of the metal when exposed only to atmosphere defined in the literature as typical of the so-called "marine-industrial" air. It is the representation of air encountered in a highly industrialized port-of-call. While materials used in the vent lines of bulk cargo carriers may be exposed to some corrosion by the vapor phase of the cargo itself, an additional factor in corrosion is generally that of the marine environment, including exhaust fumes generated by a ship's propulsion system and the industrial atmosphere to which the ship will be exposed while in port.

F. Conditions for Polymerization

The blockage of tank venting systems by polymerization of cargo can occur. Manufacturers, shippers, and users have all experienced vent blockage by the polymerization of some materials. Of the cargoes listed in subchapters D and O of Chapter 1 of CFR Title 46, thirteen cargo types have been indentified as potentially subject to polymerization. The following seven cargo types present a significant blockage hazard since they readily polymerize to a solid and require the use of an inhibitor or inert gas blanket:

- Acrylate and Methacrylate Esters
- Formaldehyde
- Acrylonitrile
- Butadiene
- Styrene
- Vinylidene Chloride
- Vinyl Acetate

Details on the polymerization conditions of these seven cargo types are given in Table 3. The remaining polymerizable cargoes are listed in Table 4 and are not expected to present a significant blockage hazard because unusual conditions are required to induce polymerization and because the polymer is a nonresinous liquid.

Many monomers that may readily polymerize are shipped with small amounts of inhibitor to prevent polymerization of the liquid cargo in the tank. Unless the monomer is held for an excessively long period of time, the inhibitor will prevent polymerization in the tank. However, we are concerned here with polymerization in the venting system after monomer evaporation and not in the liquid itself. When the cargo vaporizes, the concentration of the inhibitor is in some cases much lower in the gaseous state than is necessary to prevent polymerization. As the cargo vapors move away from the liquid and into the venting system, under these special conditions, they are essentially uninhibited.

Tables 3 and 4 list the polymerizable cargoes, their relative volatility (vapor pressure), the conditions which may initiate polymerization, and means of preventing or minimizing blockage. Appendix C provides the background information for the tables. An extensive bibliography has recently been compiled by Harman and King.⁽⁹⁾

G. Blockage from Physical Damage, Air Pollution, or Ice

1. Physical Damage

Interviews with inspectors indicate that physical damage leading to venting system blockage is usually caused by incorrect maintenance procedures. Flame screens that have been partially or completely

TABLE 3

CARGOES SUBJECT TO BLOCKAGE-CAUSING POLYMERIZATION

General Guideline: Prevent Cargo Contact with Promoters Through Proper Tank and Piping Design and Loading Practices

Cargo	Vapor Press. mm Hg at 20°C	Conditions Promoting Polymerization	Special Provisions Against Polymerization
Acrylonitrile $\text{CH}_2 = \text{CHCN}$	83	Peroxides, light, "Redox" catalysts, Azo compounds, strong bases, copper and air	Locate PV valves where cargo collection will be minimal. Inerting is recommended but not mandatory. Inspect before unloading.
Acrylate and Methacrylate Esters $\text{CH}_2 \text{COOCH}_3$	(See Appendix)	Heat, light, or catalysts - free radical initiators and strong bases - water, iron, high (above ambient) temperatures, and rust. Lack of O_2 renders the inhibitors ineffective.	For maximum safety, ullage space should be filled with dry air and vent system outlet should be covered with an air drying unit (CaCl_2 desiccant). Flame arrestor should be below and on atmospheric side of PV valve. Inspect before unloading.
Butadiene $\text{CH}_2 = \text{CHCH}=\text{CH}_2$	982	Peroxides, oxygen.	Care should be taken to insure that all air is removed from ullage space. Inspect after vapor release.
Formaldehyde Solution HCHO (30%-50% in Water)	1.3	Self polymerizing cargo. Process accelerated by acids, alkalies, and water. Temperatures below 85°F promote polymerization.	Heat venting system valves to maintain temperatures above 95°F. Inspect before unloading.
Styrene $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	6	Heat, UV light, copper, copper-bearing alloys, free radical catalysts, styrene peroxides.	Use of a PV valve will reduce vapor breathing through vent lines, reducing chances of inhibitor-free polymerization. Maintain cargo below 80°F. Inspect before unloading.
Vinyl Acetate $\text{CH}_3 \text{COOCH}=\text{CH}_2$	92	Peroxides, light, Azo compounds, "Redox" systems, organometallics, sunlight.	
Vinylidene Chloride $\text{CHCl}_2-\text{CHCl}_2$	495	Oxygen, peroxides, free-radical catalysts, light, strong bases.	Blanket ullage space with inert gas. Locate PV valve as close as possible to vent outlet. Inspect before unloading.

TABLE 4

CARGOES SUBJECT TO POLYMERIZATION WITH BLOCKAGE UNLIKELY

General Guideline: Prevent Cargo Contact with Promoters
Through Proper Tank and Piping Design and Loading Practices

<u>Cargo</u>	<u>Vapor Press. mm Hg at 20°C</u>	<u>Conditions Promoting Polymerization</u>	<u>Special Provisions Against Polymerization</u>
Acetaldehyde CH_3CHO	750	Acids, bases, oxygen	Blanket ullage space with inert gas.
Allyl Chloride $\text{CH}_2=\text{CHCH}_2\text{Cl}$	294.3	Peroxides, UV light, mineral acids, Lewis acids, aluminum, aluminum alloys, zinc, zinc alloys.	
Isobutylaldehyde $(\text{CH}_3)_2\text{CHCHO}$ and Crotonaldehyde $\text{CH}_3\text{CH}=\text{CHCHO}$	115 30	Acids, bases. See Appendix.	See Appendix.
Epichlorohydrin $\text{CH}_2\text{COHCH}_2\text{Cl}$	13	Lewis and mineral acids, bases, compounds containing labile (free) hydrogens, copper, lead, zinc, aluminum or their alloys.	
Ethylene Oxide CH_2OCH_2 Propylene Oxide $\text{CH}_3\text{CHCH}_2\text{O}$	1095 445	High temperature, alkalis, aqueous acids, ammonia, amines, organic bases, acidic alcohols, anhydrous iron, tin, aluminum chlorides, iron oxides, aluminum oxides, metallic potassium.	Refrigerate ethylene oxide cargo below 90°F.
Vinyl Chloride $\text{CH}_2=\text{CHCl}$	2580	Peroxides, Azo compounds, "Redox" systems, organometallics, sunlight.	

blocked by too-thorough paint jobs or valves with their exposed operating stems stuck by paint were reported. This appears to be due to negligence and not due to lack of understanding of the flame control devices' role: painted flame screens have been found removed from the vents or have had spikes driven through them to reopen them.

2. Air Pollution - Particulates

Airborne particulates collect on flame screens. The quantity of material that collects is dependent on many factors, including the means of unloading the cargo tank, the cleanliness of the air at the off-loading port, and the stickiness of the individual particles. Airborne particulates will only impinge upon flame screens when the tank is being unloaded or breathing in. If the particulates are not blown off and out of the venting system during loading because ullage hatches are opened, they could build up on the venting system in sufficient thickness to cause difficulty between inspections.

This problem was cited during one visit to a Coast Guard Inspection Station. The inspector noted that grain dust had stuck to flame screens used on the vessel's oil tanks. Presumably, the vessel was a grain carrier. The dust stuck to the oil that had condensed on the flame screen.

A study was conducted on this problem for a period of 14 months, during which time approximately 1.92×10^6 cubic feet of suburban air was drawn through six crimped ribbon-type flame arrestors (total area, 6.23 square inches, crimp height, .02 inches). After the 14 months, the effective flow area was reduced by only 35 percent.⁽⁵⁾ During this test, the air flow was always in one direction. There was no flushing action (such as would be encountered during loading cargo tanks) to cleanse the flame arrestors.

Thus it appears that the problem of blockage due to atmospheric pollutants is not significant enough to cause difficulty between inspections unless the atmosphere surrounding the vessel during off-loading is consistently and continuously dusty, as would be the case with grain or coal-carrying vessels, or vessels which frequently off-load in dusty ports. In these cases, the problem can be magnified by deposits of oily or sticky materials on the flame control device (as in the above example).

3. Ice Formation

During inclement and/or subfreezing weather, the possibility of blockage due to ice formation is a very real probability. Sea spray, rain water, and condensation will freeze on venting system outlets and flame screens. Any liquid that has collected inside the venting system piping can freeze into a solid plug; any condensate that may have formed on the moving parts of PV or SR valves can freeze and render the valve inoperable. Fortunately, this ice formation is not permanent, and the conditions leading up to it (cold, wet, and/or windy weather) are readily recognized. Furthermore, major activity of the venting system only occurs during loading, unloading, or gas freeing.

IV. PREVENTATIVE MEASURES

A. Objectives

Blockage occurs when narrow passages are exposed to an agent causing film buildup for sufficient time under conducive conditions to restrict flow. By reducing or interrupting any one of these factors, blockage may be minimized. There are several factors about which very little can be done in the way of prevention -- moisture collection through condensation, icing, and particulate collection. On the other hand, corrosion and cargo polymerization can be minimized by design and procedure guidelines formulated to avoid conditions presented in this report. Referring to the Fault Tree (Figure 3), note that a considerable number of blockage scenarios can be prevented if corrosion, polymerization, and crystallization are controlled.

Two other factors must be present before blockage may occur -- sufficient time and narrow passageways. By scheduling inspections at frequent intervals so that insufficient time is allowed for blockage, this hazard can be minimized for certain cargoes. Unfortunately, the data is insufficient to determine the rate of film buildup. In addition, the larger the flow passageways, the longer a given blockage mechanism will take to effect a given flow area constriction.

Any effort devoted to removing a blockage agent or interrupting any connecting line in the Fault Tree will decrease the hazard due to blockage. The sections that follow discuss some of the ways in which this may be done.

B. Loading Operations

Carelessness as a cause of blockage is difficult to regulate or control. Loading operations must be carried out so that overfilling or cargo contamination are avoided. Putting incompatible cargoes into tanks with common venting system or running the incompatible cargoes through the same lines and/or pumps may lead to polymerization or corrosion.

C. Inspection and Maintenance

The best and most effective way to minimize the blockage hazard is to inspect venting systems frequently and thoroughly enough so that significant constrictions are discovered before they have time to grow. In some cases, this means that inspections should be carried out before each unloading to insure that polymer blockage has not occurred (see Table 3). The optimum frequency is dependent on the cargo and the materials used in the venting system and can only be determined after an in-depth study of the rate of constriction of venting systems associated with each blocking agent. During inspection, any signs of corrosion should be noted; regions where dissimilar metals are joined should be especially checked for indications of galvanic corrosion.

Corroded or blocked venting system components should be replaced or repaired. Marginally affected components can sometimes be restored by flushing with fresh water and thorough drying and by removing dust, dirt, and deposits of corrosion products.

D. Materials Selection

The conditions necessary for corrosion and, to a lesser extent, for polymerization, are certain reactive combinations of vent material/cargo or vent material/atmosphere.

Considering corrosion first, Table 2 presented a matrix of the metals most commonly found in venting systems and those cargoes most likely to corrode one or more metals. If a venting system were made out of metals appropriate for specific cargoes ("A" rated combinations) and then used only for those cargoes, and if the metals also withstood the marine-industrial atmosphere, the problem of corrosion may be minimized. "Drug store" type vessels present the most severe type of service from a corrosion standpoint. Not only will the vent materials used be exposed at some time or another to cargoes which will severely corrode them, but they will be expected to withstand the possibly extreme but largely unknown corrosive action of mixtures of various cargoes over long periods of time.

Materials should be selected on the basis of their intended surroundings; that is, those expected to be at the weather end of a venting system containing a safety relief valve would be chosen from the marine-industrial column of Table 2. Those close to and in communication with the ullage space may be selected from the appropriate cargo column. If there is any doubt about a metal's suitability, the "worst case" should always be considered.

As with corrosion, some venting system materials will catalyze polymerization. In addition, some corrosion products such as rust will initiate a polymerization reaction. Appendix A or Table 3 should be consulted as to the role of various venting system metals or their corrosion products in polymerization reactions. In general, the use of reactive or catalytic metals must be avoided.

E. Special Methods to Prevent Polymerization

Appendix A details the various mechanisms by which each of the 15 potentially polymerizable cargoes can cause blockage. A set of recommendations accompanies most of these cargoes outlining the various methods of prevention. A more detailed discussion of each method is presented below.

1. Use of a Pressure-Vacuum Valve and Its Location

As previously mentioned, the vapor of an inhibited cargo can polymerize in the venting system in special conditions where, due to selective evaporation, the concentration of the inhibitor is insufficient to stop the reaction in the vapor phase. This situation can be controlled by inerting or by using an inhibitor with adequate volatility.

In order to control some cargoes which more readily polymerize in the presence of moisture, oxygen, light, or certain air pollutants, it is recommended that the PV valve be located at the venting system outlet (weather end). This will minimize the quantities of

these air-borne initiators that will enter the venting system and promote polymerization.

2. Use and Location of Flame Control Devices

Some polymerizable cargoes such as formaldehyde are difficult to keep from blocking flame control devices and are also flammable. Surprisingly, some cargo manufacturers recommend that flame control devices not be used for these materials, feeling that the problems due to blockage are more troublesome than those due to fire! One way around this problem is as follows: The devices can be used and heated with steam, which may reduce or eliminate the danger of polymerization and crystallization (such is the case with formaldehyde and naphthalene, respectively).

If frequent inspections for blockage can be made and if facilities for removing such blockage are available, the use of tandem flame arrestors is recommended.⁽⁶⁾ When connected to the vent piping by a three-way valve, one unit may be removed from service and cleaned while the other arrestor is providing protection. The three-way valve insures that at least one arrestor will always be in service and that at no time will the venting system be shut off by the valve.

F. Inter-Cargo Compatibility

Many polymer-forming reactions are catalyzed or initiated by other chemicals or compounds which could conceivably be carried aboard the same vessel. (See Appendix A or Table 3.) It is obviously important that these cargoes be kept isolated from each other. The subsequent use of the same pumps must also be avoided unless they are thoroughly cleaned before and after handling each cargo.

G. Mechanical Design

Besides judicious placement of valves and flame control devices and large flow passages, other mechanical methods may be incorporated into venting systems to minimize the blockage hazard. Moving parts are subject to sticking by one or more blockage mechanism. Low points offer collecting points for cargo or other foreign material. Eliminating these from venting systems may help to minimize blockage.

The venting system can be designed to facilitate safety inspections with clean-out doors and inspection parts within convenient reach.

Atmospheric factors, such as rain, sea spray, icing, and, to some extent, particulates, can be excluded from venting systems by placing weather heads over the vent outlets, using goosenecks where permissible and locating the vent outlets amidships (but away from exhaust stacks).

Human factors such as paint can be minimized by placing paint brush proof guards over flame control devices or recessing them a short distance in from the end of the pipe and putting a simple cross at the end of the pipe (Figure 4).

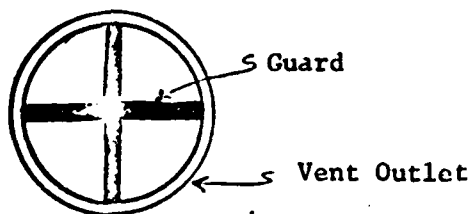


FIGURE 4
Paint Brush Guard

As mentioned previously, large flow passage areas take longer to block because of the greater film thicknesses required to cause an 85% or greater constriction. Therefore, the blockage hazard may be minimized by utilizing venting system devices with the largest possible flow passage diameters.

From section IIA, it should also be apparent that the greater the venting system flow velocity, the less area constriction required to produce a given pressure drop. Therefore, venting systems designed with low flow velocities offer the minimum safety hazard due to blockage.

V. UNANSWERED QUESTIONS

The findings reported herein are mainly on corrosion and polymerization, two of the causes most often cited for blockage. It must be emphasized that much more information about blockage must be gathered before the relative importance of these two causes can be assessed, the overall blockage risk estimated in comparison to other risks, or cost effective prevention methods or regulations adopted. The following questions remain:

1. Which components of the vent system are most often blocked or partially blocked?

2. Which cargoes cause the most blockage incidents for a given number of tank loadings?

3. What area constriction leads to tank failure? We know that venting systems designed with 10 fps flow and negligible pressure drop need a single flow area restriction of 94% or more before the tank pressure will exceed 1 psig. While this is indicative of the allowable blockage under normal operating conditions, a less severe reduction may not accomodate abnormal venting rates under emergency fire conditions. On the other hand, 1 psig may be below the stress limit of some tank designs. This question will be looked at more closely in Tasks III and IV of the subject contract.

4. What are the most prevalent modes of blockage? Marine inspectors can identify only a few types of blockage. Human-caused blockage, some types of corrosion, and some cargo deposition, as well as mechanical faults, are readily identified. On the other hand, combinations of these blockage mechanisms may cause material buildup on venting system components, or blockage modes which have not been recognized may be important. The appearance of a dark solid may not be the result of simple corrosion but may have been caused by a cargo reacting with the vessel's exhaust gases, for instance. It is therefore difficult, if not impossible, to completely characterize the causes of blockage at this point. The relative importance, frequency, or rate of blockage due to different mechanisms is unknown. The most severe examples may not be uncovered since components may be destroyed if blockage leads to tank failure.

5. What is the overall risk of blockage? Is it extremely rare or does it cause tank failure with some regularity? Does it cause more or less damage than fires and other hazards?

If the above questions can be answered, the following goals may be realized:

1. Inspections may be carried out at the most cost-effective frequency for each type of venting system and/or cargo.
2. Venting systems may be designed with the most cost-effective materials.
3. Venting systems may be designed with the greatest flexibility from a manifolding, material, and cargo compatibility standpoint.
4. Inspections can be more efficiently carried out as inspectors would know exactly what to look for and where to find it, depending upon the cargo history of the vessel.

References

1. Harrington, Roy L., Marine Engineering, The Society of Naval Architects and Marine Engineers, New York, 1971, p. 707.
2. Case Histories of Accidents in the Chemical Industry, Volumes I, II and III and their supplements. Manufacturing Chemists Association, Washington, DC.
3. Equipment Specifications - U-100 Protectoseal Tank Fittings and Safety Devices for Fire Prevention, Environmental, and Vapo-Control, The Protectoseal Company, Bensenville, Illinois, 1973.
4. Pressure Relieving Systems for Marine Cargo Bulk Liquid Containers, National Academy of Sciences, Washington, DC, 1973.
5. Rogowski, Z. W., Field Trials to Assess the Blockage of Arrestors by Atmospheric Pollution, Fire Research Note 786, Fire Research Station, Borehamwood, Herts, England.
6. Handbook of Industrial Loss Prevention, Factory Mutual Engineering Corporation, McGraw-Hill, New York, 1967.
7. Martin, W. S., "A New Approach to Gas Venting of Tankers", Trans RINA 112 p.307 (1970).
8. Shapiro, A. H., The Dynamics and Thermodynamics of Compressible Fluid Flow, Vol. I, p.83 ff, Ronald Press, New York, 1953.
9. Harman, M. and King, J., "A review of violent monomer polymerization: a selected literature survey", Operations Research, Inc., Contract CCT-46-74-74 for National Research Council (1974).

APPENDIX A

Selected Case Histories of Venting System Failure Due to Blockage

The following collection of reported tank failures were the result of venting system plugging and corrosion as reported to the Manufacturing Chemists Association.⁽²⁾ These represent less than 1% of all reported industrial accidents from 1962 through 1973.

CASE HISTORY NO. 172

**Plugged Flame Arrestor --
Explosion -- No Injury**

Description: Introduction of caustic into mixture of raney nickel and water caused boiling which built up pressure in a normally low pressure vessel and an explosion resulted. There was no fire or injury.

Cause: Explosion occurred because flame arrestor in the 4-inch vent line was completely plugged due partly to corrosion and partly to catalyst.

Preventive Measures: An 8-inch vent has now been installed without flame arrestor; in lieu of the latter the operation is blanketed with steam. A regularly scheduled inspection routine on other such flame arrestors has been initiated.

CASE HISTORY NO. 687

Faulty Valves and Lack of Eye Protection

Description: An employee was filling a cavity in front of #6 Sulfur Furnace with a type of acid cement. This was being pumped under 20 pounds pressure. He shut off the pump and opened a relief valve in the line to bleed off the pressure. This was done so that he could break the line at a union near the front of the furnace. As he attempted to break the line, the material sprayed out hitting him in the eyes and face. He was not wearing eye protection and the cement entered his eyes causing severe abrasions of both corneas with severe conjunctivitis secondary to the injury.

Cause: Investigation revealed that the nipple on the relief valve was frozen shut and failed to bleed off the pressure when it was opened. Also a valve ahead of the union could not be completely closed because of the cement setting up on the valve seat. As a result of these two valve failures, line pressure was on the union when he cracked it allowing the material to spray out.

Preventive Measures: 1. Employees have been informed of this accident and again instructed to wear eye protection.

2. During cold weather valves will be kept warm and operable with the use of propane heaters.

CASE HISTORY NO. 882

Polymer Plugged System-- Pressure Indicator Fails

Description: Just prior to the time of this incident, a separator was being tested for leaks by use of high pressure. The pressure had then been released using normal venting procedures and the pressure gauges on the test panel board indicated zero pressure. A pipefitter loosened the high pressure tubing connections and found no indication of residual pressure. As he bent over to complete the disconnection of the tubing, there was a mechanical failure of a fitting in the system. The stream of test oil struck his leg and knocked him down. The pressure continued to be released intermittently, forcing the man to crawl out of the area in order to avoid being struck by the swinging high pressure tubing. The pipefitter received a serious laceration of the leg, but was able to return to work the same day.

Cause: The plugging of the system with polymer from the test item was the direct cause of the incident. This polymer held pressure in the system in such a way that the gauges did not indicate that pressure existed.

Preventive Measures: 1. Piping system is to be revised to provide another pressure indicator and an additional method of venting.

2. The entire system has been completely inspected and cleaned, and in the future, items to be tested will be cleaned prior to testing.

CASE HISTORY NO. 1091

Fume Release from Pipeline

Description: Maintenance operating personnel were checking a corrosive liquid product pipeline to determine the reason for a block in the line. (Refer to sketch) V-1, v-2, v-3, v-4 were closed and v-5 was open. From a platform on top of code 27 above flange No. 2, the employee proceeded to open flange No. 2. Three bolts had been removed from flange No. 2 and when the last and fourth bolt was loosened, there was a "puff" of irritating fumes that came from the opening and struck the employee in the face. The employee had to make his exit through a fumigated area due to the wind direction at the time.

Cause:

1. Employee did not wear the personal protective equipment required.
2. The vent system was blocked up and under a slight amount of pressure.
3. Failure of employee to attempt to bleed pressure from the pipeline prior to starting the work.

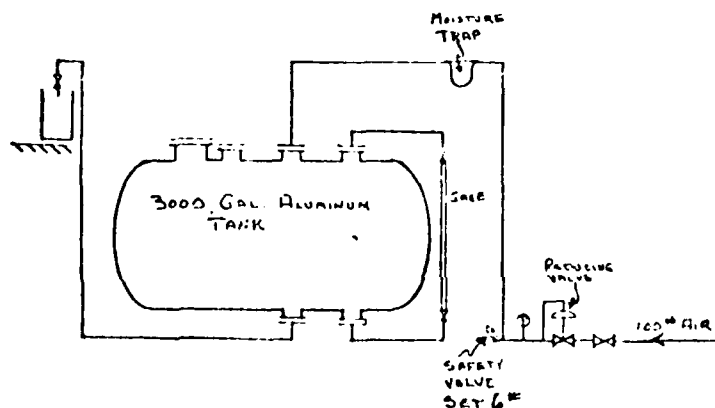
CASE HISTORY NO. 1912

The LOCATION of the Safety Valve is Also Very Important

Description: A 3000 gallon aluminum tank was being used for 56% Acetic Acid service. It was pressurized with 6 pounds of air to force it through overhead lines to the dispensing locations inside the building. The Safety Valve was located on an elbow right next to pipe tee with a vertical riser of about 6 feet. The moisture trap was on the horizontal line.

The scale, dirt, and moisture from the vertical pipe and the horizontal run was driven into the elbow and the Safety Valve opening each time the system was pressurized. Finally the elbow and valve became plugged so that when the Reducing Valve leaked, the Safety Valve could not function. One head was blown out of the tank with enough force to remove 1000 square feet of window, a portion of the roof, and the brick chimney of the adjacent building. Fortunately the injuries were minor but the property damage was extensive.

Preventive Measure: A Safety Valve should be located to minimize the amount of foreign material that can accumulate in its fitting or entrance. In this case it could have been off a tee in the vertical riser, or at the top of the riser. Such valves should be removed and the valve and fittings checked on a periodic basis.



CASE HISTORY NO. 1192

Monomer Tank Overflow

Description: After gauging storage tank for adequate outage, a pump operator hooked up a tank wagon containing volatile monomer and pumped the contents into a tank. During the pumping operation, the operator stood by the pump and trailer. However, the vent pipe at the tank was plugged causing the monomer to flow out of the dip leg, losing approximately 13,127 lbs.

Cause: The vent pipe on the monomer tank was plugged with polymer causing the liquid to overflow from the dip leg. The tank capacity was 10,000 gallons. It had 2,000 gallons in it and the new delivery was 4,300 gallons.

Preventive Measures: The vent pipe was unplugged and the flame arrestor checked. "Production" will inspect and clean the vent on a regular routine schedule. Redesign of the dip leg on the storage tank will be investigated.

CASE HISTORY NO. 1604

Over-Pressurization of Tanker

Description: The road tanker arrived at the works carrying 6 tons of hydrochloric acid (28°TW). It was a two compartment tanker and had been initially loaded with 12 tons of hydrochloric acid. The front compartment containing 6 tons had been discharged at another works that morning without difficulty. On arrival, the tanker driver was directed to the appropriate section where he reported to the foreman who gave permission to discharge the remaining hydrochloric acid to the storage. The delivery point was unlocked and the driver was then left to couple up the tanker on his own.

(The hydrochloric acid bulk storage for this plant is outside the door of the building and on the opposite side of the roadway. The road is a cul-de-sac and tankers back up to the discharge point. The 2-1/2 in. delivery line to the storage tank terminates in a Saunders valve and a padlocked blank flange at a height of 41 in. above the footpath. The storage is permanently vented to an absorber.)

To couple up the tanker, the driver connected a hose to the rear compartment and to the delivery line to the storage boiler. He then opened the valve on the delivery line, the valve on the outlet pipe from the rear compartment of the tanker, and, ostensibly the foot valve of the rear compartment. He then opened the air feed valve to the rear compartment and started up the air compressor, which was driven by the tanker's engine.

After a period of time estimated by the driver as 5-10 minutes, he heard air escaping at the top of the tanker so he climbed up to investigate. He found that air was escaping from the air release valve at the front of the tanker and closed this valve. Almost immediately after this, while the driver was still standing on the top of the tanker just to the rear of the air release valve he had closed, the lid blew off the front compartment of the tanker. It landed on the roof of another building (about 55 ft. high and 33 yd. from the tanker's position).

The driver climbed down from the tanker at the rear and stopped the compressor and went to the Medical Centre where he was treated for shock. When he returned to the vehicle he realized that no acid had been blown out of the rear compartment (this was confirmed by dipping the storage boiler), so he released the pressure in the rear compartment. It was later established that the foot valve on the rear compartment was faulty.

Cause: The circumstances of the incident were fully investigated by a Committee of Enquiry and it was concluded that the most likely cause of the incident was a combination of circumstances: a partial blockage of the relief valve leading to overpressurization of the tank together with insecure fastening of the lid, probably as a result of poor design.

Preventive Measures: The operation and maintenance of bulk delivery vehicles is the responsibility of the transport contractor. The responsibility of the works is primarily to ensure safe access to a safe discharge point and to make adequate capacity available to contain safely the whole contents of the tank being discharged.

APPENDIX B

Bibliography for Corrosion

General

1. Stauffer Chemical Co., Industrial Chemical Division, 380 Madison Avenue, New York, NY 10017.
2. Reinhold Publication, Mid-September, 1971 Materials Selector Issue, Volume 74, Number 4.
3. "Metal Corrosion in the Atmosphere," ASTM (STP 435), Boston, Massachusetts, June, 1967.
4. M. G. Fontana, N. D. Greene, Corrosion Engineering, McGraw Hill Book Co., 1967.
5. Uhlig, H. H., Corrosion and Corrosion Control, John Wiley & Sons, Inc., New York, 1963.
6. M. G. Fontana, R. W. Staehle, Advances in Corrosion Science & Technology, Volume 4, Plenum Press, New York, 1974.
7. C. J. Smithells, Metals Reference Book, 4th Edition, Plenum Press, 1967.
8. F. L. Laque, H. R. Copson, Corrosion Resistance of Metals and Alloys, 2nd Edition, Reinhold Publishing Corp., 1963.
9. H. O. Teeple, Corrosion by Some Organic Acids and Related Cpds., N.A.O.C.E., Volume 8, pp. 14-28, January, 1952.

Copper, Bronzes, and Brasses

1. H. Leidheiser, Jr., The Corrosion of Copper, Tin and Their Alloys, John Wiley & Sons, Inc., 1971.
2. Chemical Engineering, pp. 108-112, January 1951.
3. C. W. Hummer, Jr., C. R. Southwell, and A. L. Alexander, Materials Protection, pp. 41-47, January, 1968.
4. C. R. Southwell, A. L. Alexander and B. W. Forgeson, Corrosion of Metals in Tropical Environments, Volume 14, pp. 55-59, December, 1958.
5. B. W. Forgeson, C. R. Southwell, A. L. Alexander, H. W. Mundt, and L. J. Thompson, Corrosion of Metals in Tropical Environments, Volume 14, pp. 34-41, February, 1958.
6. A. L. Alexander, C. R. Southwell, and B. W. Forgeson, Corrosion of Metals in Tropical Environments, Volume 17, pp. 97-104, July, 1961.

7. C. R. Southwell, B. W. Forgeson, and A. L. Alexander, Corrosion of Metals in Tropical Environments, Volume 16, pp. 120-126, October, 1960.
8. B. W. Forgeson, C. R. Southwell, and A. L. Alexander, Corrosion of Metals in Tropical Environments, Volume 16, pp. 87-100, March, 1960.

Also see General References 3 and 4.

Steels: See General References 3, 5, 6, and 7

Cast Iron: See General References 4, 5, and 8

Stainless Steel: See General References 4, 6, 7, and 8

Nickel, Monel, Inconel, and Hastelloy

1. Charles R. Southwell, Allen L. Alexander, Materials Protection, pp. 39-44, March, 1969.
2. B. W. Forgeson, C. R. Southwell, A. L. Alexander, H. W. Mundt, and L. J. Thompson, Corrosion of Metals in Tropical Environments, Volume 14, pp. 34-41, February, 1958.
3. C. R. Southwell, B. W. Forgeson, and A. L. Alexander, Corrosion of Metals in Tropical Environments, Volume 14, pp. 55-59, September, 1958.
4. Morgan M. Hoover, "Alcohol vs. Construction Materials," Chemical Engineering, November, 1957.
5. A. L. Alexander, C. R. Southwell, and B. W. Forgeson, Corrosion of Metals in Tropical Environments, Volume 17, pp. 97-104, July, 1961.
6. B. W. Forgeson, C. R. Southwell, and A. L. Alexander, Corrosion of Metals in Tropical Environments, Volume 16, pp. 87-100, March, 1960.

Also see General References 4, 5, 6, 8, and 9.

Aluminum and Its Alloys

1. Kent R. Van Horn, Aluminum, Volume I, American Society for Metals, A.S.M., 1967.
2. C. R. Southwell, A. L. Alexander, and C. W. Hummer, Jr., Materials Protection, pp. 30-35, December, 1965.
3. F. W. Fink, et al., The Corrosion of Metals in Marine Environments, N.T.J.S., May, 1970.
4. W. G. Lloyd, F. C. Taylor, Jr., Industrial and Engineering Chemistry, Volume 46, No. 11, pp. 2407-2416, November, 1954.

See also General References 4, 5, and 9.

Magnesium

1. C. Sheldon Roberts, Magnesium and Its Alloys, John Wiley & Sons, Inc., 1960.
2. C. R. Southwell, Allen L. Alexander, and C. W. Hammer, Jr., Materials Protection, pp. 30-35, December, 1965.

See also General References 4, 5, 6, 7, and 8.

Lead

1. F. W. Fink, et al., The Corrosion of Metals in Marine Environments, N.T.I.S., May, 1970.

See also General References 4, 5, 7, 8, and 9.

Styrene

Styrene Monomer, Storage and Handling, Technical Service Bulletin, Monsanto Company, St. Louis, Missouri.

Butadiene

Butadiene Materials Safety Data Sheet, Exxon Chemical Co., Houston, Texas.

Ethylene Oxide

Ethylene Oxide Handling Manual, BASF Wyandotte Corp., Wyandotte, Michigan, 1972.

Propylene Oxide

Propylene Oxide Technical Brochure, Jefferson Chemical Co., Inc., 1962.

APPENDIX C

Detailed Findings on Polymerization of Thirteen Specific Cargo Types

This appendix presents a summary of the background data used to compile Tables 3 and 4. In addition, each summary contains more detailed recommendations than outlined in the table. These are made to provide the Coast Guard with guidelines for the maximum protection against blockage by polymerization. This information has been assembled from a review of manufacturers' technical brochures, Manufacturing Chemists Association Material Safety Data Sheets, as well as the generally known reactivity of these especially polymerizable cargoes.

ACETALDEHYDE

A. Reactivity

1. Polymerization

Acetaldehyde polymerizes in the presence of acids or bases. For example, a trace of a mineral acid such as sulfuric acid converts the aldehyde to a trimer, paraldehyde. However, paraldehyde is a liquid (b.p. 124°C) and therefore should not cause permanent blockage. Dilute or weak bases can promote a condensation reaction that similarly yields liquid products. However, under certain conditions these condensation products can condense further to produce resinous materials. Solid resins are produced in the presence of concentrated strong bases. These resins can cause vent blockage.

2. Oxidation

Acetaldehyde is easily oxidized in the presence of air to peroxides and acetic acid. The former is explosive, and the latter is corrosive. Consequently, storage tanks should be blanketed with an inert gas such as nitrogen.

B. Present Requirements

Acetaldehyde liquid is shipped under pressure in a tank fitted with a safety release valve. The space above the tank contains an inert gas. The special requirement section [151.55-1(h)] stipulates that alkaline or acidic materials such as caustic soda or sulfuric acid should not be allowed to contaminate this cargo.

C. Recommendations

None.

ACRYLONITRILE

A. Reactivity

1. Polymerization

Acrylonitrile, as shipped, contains inhibitors to prevent polymerization. Acrylonitrile polymerizes in the presence of peroxides, light, "redox" catalysts, azo compounds, and strong bases. In the absence of inhibitors, acrylonitrile is subject to self-polymerization, especially at temperatures above 470°K. Furthermore, once polymerization is initiated, it is autocatalytic and exothermic (Heat of polymerization 17.3 kcal/mole).

B. Present Requirements

Acrylonitrile liquid is shipped at atmospheric pressure in a tank fitted with a pressure-vacuum venting valve. The special requirement section stipulates that copper and copper-bearing alloys should not be used as materials of construction for tanks, pipelines, valves, fittings, and other items of equipment that may come in contact with the cargo liquid or vapor.

C. Recommendations

Because acrylonitrile vapor, free of inhibitor, could condense and become trapped in the vent line if the venting valve is caused to open during shipment, we recommend location of the pressure-vacuum valve so that the collection of the acrylonitrile vapor is minimized. The vent line should be as short as possible.

Cargo should not be allowed to contact peroxides, "redox" catalysts, azo compounds, and strong bases.

For maximum safety, it would be advisable to ship the acrylonitrile under a nitrogen atmosphere, and the valve and flame control device should be inspected before unloading.

ACRYLATE AND METHACRYLATE ESTERS

A. Reactivity

1. Polymerization

Acrylates polymerize in the presence of heat, light or catalysts -- both free radical initiators and strong bases act as catalysts. Acrylates, as shipped, contain inhibitors to prevent polymerization during storage. Generally, these are phenolic inhibitors, and the effectiveness of phenolic inhibitors is dependent upon the presence of oxygen. For this reason, acrylic monomers must always be stored in contact with dry air.

The exclusion of moisture is of utmost importance, because it tends to promote the formation of "popcorn" polymer, which is hard, granular, and insoluble. Popcorn polymer formation is promoted by lack of oxygen, water contamination, iron contamination, and elevated temperatures. If it forms in the vents, valves, and flame arrestors, it can cause blockage.

Ethylacrylate, which is the most reactive acrylate listed among the cargoes in Table 151.05 in the regulations (46 CFR) has shown the greatest tendency toward popcorn polymer formation. Methyl methacrylate and the higher-boiling acrylates are somewhat less reactive. In the absence of inhibitors, ethyl acrylate and methyl methacrylate will self-polymerize above 10°C (50°F). The polymerization is auto catalytic with the evolution of heat (18.6 kcal/mole for methyl acrylate and 12.5 kcal/mole for methyl methacrylate).

The accumulation of a water layer in any part of a steel storage tank may cause rusting. Polymerization may then be initiated by the rust particles in contact with monomer and water.

The relative volatility of these esters is shown below:

<u>Monomer</u>	<u>b.p. (°C)</u>
n-butyl acrylate	145.7 - 148.0
isobutyl acrylate	135 - 137
methyl methacrylate	100.3 - 100.8
ethyl acrylate	98.8 - 99.8

Acrylate and Methacrylate Esters

B. Present Requirements

These materials are liquids that are shipped in tanks fitted with pressure-vacuum venting valves.

C. Recommendations

To minimize the passage of inhibitor-free cargo vapors into the venting system, the PV valve should be located as close to the tank as possible and where liquid cargo condensate will not collect. However, should the valve open during shipment or loading, inhibitor-free cargo vapors would travel into the vent lines where they would be exposed to moisture and rust. Therefore, the vent lines should be made of corrosion resistant materials such as stainless steel. In any event, the vent lines should be as short as possible so that the vapors may travel completely through the vent with a minimum residence time.

The flame control device should be located below and on the atmospheric side of the PV valve to minimize the vapor contact time and allow any cargo condensate to drain through the device and out of the system.

For maximum safety, the ullage space should be blanketed with dry air. Cargo should not be allowed to contact free-radical initiators, water, iron, rust, or strong bases.

As an alternative to the above, the venting system should be inspected before unloading the cargo.

ALLYL CHLORIDE

A. Reactivity

1. Polymerization

In the presence of peroxides, ultraviolet light, mineral acids, or Lewis acids such as ferric chloride and aluminum chloride, allyl chloride is polymerized to low-molecular-weight liquid polymers. Resinous materials are generally not produced. During storage, allyl chloride can produce small amounts of hydrochloric acid, which is very corrosive. If iron oxide is present in the tank, the HCl can form iron chloride compounds that promote the condensation of allyl chloride to high-boiling liquids. In general, because allyl chloride is reactive, it should not come in contact with aluminum, aluminum alloys, zinc, or galvanized metal.

B. Present Requirements

Liquid allyl chloride is shipped in a tank that is fitted with a pressure-vacuum venting valve.

C. Recommendations

Avoid aluminum, zinc, and their alloys as materials of construction that may come in contact with the cargo liquid or vapor because these could combine with HCl to produce Lewis acids.

Cargo should not be allowed to contact peroxides, mineral or Lewis acids, or iron oxide.

BUTADIENE (INHIBITED)

A. Reactivity

1. Polymerization

Butadiene, as shipped, contains inhibitors to prevent polymerization. In the absence of these inhibitors, butadiene will polymerize at room temperature to a hard resinous material. This reaction releases heat. The reaction is promoted by oxygen in the air through the formation of reactive peroxides. The "popcorn" polymer that is produced can plug valves, vents, pumps, pipelines, etc. Butadiene also forms a liquid dimer during storage, but this should not cause significant vent blockage.

Butadiene does have a documented history of causing blockage in vent systems by polymerization.*

B. Present Requirements

Butadiene gas is shipped under pressure in a tank fitted with a safety relief valve.

C. Recommendations

During loading, efforts should be made to insure that all air is expelled from the storage tank. Inspect after each venting system use.

*Butadiene: Manufacturing Chemists Association, Material Safety Data Sheet.

BUTYRALDEHYDES AND CROTONALDEHYDE

A. Reactivity

1. Polymerization

These aldehydes can polymerize in the presence of acids or bases, but hard resinous products are not formed. The resulting polymers are liquids; therefore, blockage of vents is unlikely.

2. Oxidation

In the presence of air, these aldehydes will yield acids that are corrosive to steel. Crotonaldehyde is most reactive, butyraldehyde is least, and isobutyraldehyde is intermediate in reactivity.

B. Present Requirements

These liquid aldehydes are shipped at atmospheric pressure in tanks that are fitted with pressure-vacuum venting valves. The special requirement section stipulates that alkaline or acidic materials should not be allowed to contaminate this cargo.

C. Recommendations

To maintain the quality of the aldehydes and reduce corrosion, the use of a blanket or inert gas over the cargo tank and in the vent line is advisable, and the venting valve should be located as close to the vent outlet as possible.

For maximum safety, low points or horizontal runs should be fitted with drains to remove any liquid polymer that may collect.

EPICHLOROHYDRIN

A. Reactivity

In the presence of catalysts such as Lewis or mineral acids, bases, and compounds having labile hydrogens, epichlorohydrin polymerizes into materials that vary in nature from light mobile liquids to highly viscous ones. With special catalyst systems, epichlorohydrin can yield very high molecular weight polymers that are elastomeric in nature.

Copper, lead, zinc, aluminum, and their alloys can react with the active chlorine in epichlorohydrin to form metal chlorides. These metal chlorides can in turn act as Lewis acids which can catalyze the formation of viscous polymers that could cause blockage.

B. Present Requirements

Liquid epichlorohydrin is shipped in a tank that is fitted with a pressure-vacuum venting valve.

C. Recommendations

Avoid the use of copper, lead, zinc, or aluminum or their alloys in the vent lines and valves.

The cargo should not be allowed to contact Lewis acids, mineral acids, bases, copper, lead, zinc, aluminum, or their alloys.

ETHYLENE AND PROPYLENE OXIDES

A. Reactivity

These oxides polymerize by a reaction that involves the opening of the epoxide ring. The reaction is exothermic and can be self catalytic leading to explosions, especially in the case of ethylene oxide. The following conditions promote the polymerization reaction: high temperatures, alkalies, aqueous acids, ammonia, amines, and organic bases, acidic alcohols, anhydrous iron, tin and aluminum chlorides, iron and aluminum oxides, and metallic potassium. In general, these catalysts yield polymers that vary in nature from light mobile liquids to highly viscous ones. Though these oxides can yield solid polymers, these only form under highly controlled conditions, such as high temperature (700°K) and with very unique organometallic catalysts. Consequently, blockage by these polymers is not likely to occur. However, the reaction can lead to an explosion if a hot spot is present.

B. Present Requirements

Both ethylene oxide and propylene oxide are shipped under an inert atmosphere (to reduce the explosive hazards) in tanks equipped with safety release valves. Ethylene oxide is shipped in a cargo tank that is equipped with refrigeration to maintain the cargo temperature below 90°F. The special requirements section indicates that mercury, silver, aluminum, magnesium, copper, and their alloys shall not be used for any valves, gages, thermometers, or similar devices and that the outlets of each vent riser shall be fitted with acceptable corrosion-resistant flame screens to avoid rust that can catalyze the polymerization reaction.

C. Recommendations

Cargo should not be allowed to contact alkalies, aqueous acids, ammonia, amines, organic bases, acidic alcohols, anhydrous iron, tin, aluminum chlorides, iron oxide, or metallic potassium. Hot spots should be avoided.

FORMALDEHYDE SOLUTION, 37 - 50%

A. Reactivity

Formaldehyde gas is very reactive and will self polymerize in the absence of catalysts. Even the purest material will show signs of polymerization after 4 hours at temperatures as low as -80°C. Polymerization is powerfully accelerated by traces of acids, alkalies, and water. The completely anhydrous gas is relatively stable under atmospheric pressure at temperatures of 80-100°C.

Formaldehyde polymers are white solid materials. Paraformaldehyde is one of the common polymers that form very readily into a solid material that can easily cause blockage.

This cargo has a history of causing blockage by polymerization.*

B. Present Requirements

Formaldehyde is a gas at ordinary temperatures and is shipped in aqueous solutions containing 37-50% of dissolved formaldehyde gas and is stabilized against polymerization with 6 to 12% methanol. The solution is shipped in a tank vented through a pressure-vacuum valve. The special requirement section indicates that alkaline or acidic materials should not be allowed to contaminate this cargo.

C. Recommendations

Because formaldehyde gas forms solid polymers very rapidly, and because formaldehyde gas exists in the atmosphere above the cargo tank and in the vent line below the pressure-vacuum valve, blockage of the vents and valves is difficult to prevent. One formaldehyde manufacturer indicated that the only way to eliminate the possibility of blockage is to heat the vent system to maintain temperatures above 95°F.* The polymer can be easily removed by washing the valves with hot water or aqueous ammonia.

Cargo should not be allowed to contact water.

Venting system should be inspected before unloading.

* Telephone communication, Mr. Croft, Product Information, EI duPont de Nemours & Co., Wilmington, Delaware, January 21, 1975.

STYRENE

A. Reactivity

In the absence of an inhibitor (usually phenols), pure styrene polymerizes slowly at room temperature and more rapidly under warmer conditions (Activation energy 20.8 kcal/mole) to yield a solid polymer. The polymerization reaction is promoted by free-radical catalysts such as peroxides, as well as UV light. Self polymerization can be autocatalytic because the reaction is quite exothermic (17.6 kcal/mole). The inhibitor TEC is consumed as it performs its function and should be checked every few days.

Oxygen tends to degrade styrene and forms styrene peroxides. These peroxides will promote the polymerization reaction. However, some oxygen is necessary for the effective action of the inhibitor. Therefore, styrene is usually not stored under a blanket of an inert gas.

Copper and its alloys in contact with styrene produce contaminants that also can promote the polymerization reaction.

This cargo has a history of causing blockage by polymerization.*

B. Present Requirements

Liquid styrene monomer is shipped in a cargo tank with open venting but with a flame control device.

C. Recommendations

Because styrene vapor, free of inhibitor, can condense and become trapped in the vent system and form solid plugs of polymer, we recommend the use of a pressure-vacuum valve close to the vent outlet to minimize the breathing of air into the vent system. If the styrene is transported in tropical climates where temperatures in excess of 80°F are common, the cargo tank should be refrigerated.

The flame arrestor, PV valve, and vent system piping should be inspected as frequently as feasible. Furthermore, the flame control devices and PV valves should be so located that they may easily be inspected and cleaned.

Cargo should not be allowed to contact copper or its alloys or peroxides.

Venting system should be inspected before unloading.

* Styrene: Manufacturing Chemists Association, Safety Data Sheet.

VINYL ACETATE

A. Reactivity

Vinyl acetate as shipped contains inhibitors (usually hydroquinone) to prevent polymerization. The polymerization is promoted by peroxides, light, azo compounds, and "redox" catalysts. In the absence of inhibitors, vinyl acetate is subject to self polymerization, which is exothermic (21 kcal/mole) and autocatalytic. If transported at cool temperatures, excluding light, and inhibited, then vinyl acetate is storable up to 6 months without polymerization (essentially stable).

A common impurity in vinyl acetate is acetaldehyde, which is formed by the reaction of vinyl acetate and water (hydrolysis). Acetaldehyde can be troublesome under storage conditions because it is easily oxidized in the presence of air to a peroxide. And, in turn, the peroxide can decompose and promote the polymerization of vinyl acetate. Vinyl acetate polymers vary in nature from liquids to greases and solids.

B. Present Requirements

Vinyl acetate liquid is shipped at atmospheric pressure in a tank that is fitted with a pressure-vacuum venting valve.

C. Recommendations

Because vinyl acetate vapor, free of inhibitor, could condense and become trapped in the vent line if the venting valve is caused to open during shipment, we recommend location of the pressure-vacuum valve close to the outlet of the vent to minimize the collection of vinyl acetate on the atmospheric side of the vent line.

The cargo should not be allowed to contact peroxides, azo compounds, "redox" catalysts, or water.

Although with proper cooling and inhibition vinyl acetate is stable, for maximum safety, we recommend the use of a blanket of dry inert gas over the vinyl acetate in the tank and recommend that precautions should be taken to avoid water contamination of the acetate. These measures will reduce the chances for forming aldehydes and peroxides that will induce polymerization.

The vent system should be inspected as frequently as feasible and at least every 6 months.

VINYL CHLORIDE

A. Reactivity

Vinyl chloride is usually transported over land with no inhibitors; however, most vinyl chloride that is transported by water contains small amounts of inhibitors (usually phenolic derivatives). Vinyl chloride polymerizes in the presence of catalysts such as peroxides, azo compounds, "redox" systems, organometallics, or sunlight. Vinyl chloride forms unstable peroxides in the presence of oxygen. If polymers are formed, they are usually solid materials. The polymerization reaction is exothermic (22.9 kcal/mole).

B. Present Requirements

Vinyl chloride is a gas at ambient temperatures and a liquid at low temperatures (b.p. -13.8°C , 7°F). It is shipped either as a gas under pressure in a tank fitted with a safety-release venting valve or as a liquid in a refrigerated cargo tank fitted with a pressure-vacuum venting valve. The use of copper, aluminum, magnesium, mercury, silver, and their alloys is disallowed as materials of construction for the storage system.

C. Recommendations

Cargo should not be allowed to contact peroxides, azo compounds, "redox" systems, or organometallics.

VINYLDENE CHLORIDE

A. Reactivity

Vinylidene chloride, as shipped, contains inhibitors such as hydroquinones or substituted phenols to prevent polymerization. Uninhibited vinylidene chloride, in the presence of oxygen or air, forms a complex peroxide compound, which is violently explosive (18 kcal/mole), at temperatures as low as -40°C . This peroxide and other free-radical catalysts can initiate a polymerization reaction that produced a hard solid material, which can cause blockage of vents and valves. The polymerization reaction also is initiated by light and strong bases.

B. Present Requirements

Vinylidene chloride liquid is shipped in a cargo tank vented through a pressure-vacuum venting valve and a flame arrestor. All vapor space above the cargo tank is filled with a gas (other than air) that will not react with the cargo. Furthermore, aluminum or copper or their alloys cannot be used as materials of construction for the tanks, the valves, or the piping system.

C. Recommendations

Because vinylidene chloride vapor, free of inhibitor, could condense and become trapped in the vent line and the valves, if the venting valve is caused to open during shipment, we recommend location of the pressure-vacuum valve as close to the exit of the vent as possible to minimize the collection of uninhibited vinylidene chloride on the atmospheric side of the PV valve.

Cargo should not be allowed to contact peroxides or strong bases.

Venting system should be inspected before unloading.